Photothermal Speckle Modulation for Materials Characterization*

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Abstract

We have developed a non-contact, photothermal materials characterization method based on visible-light speckle imaging. This technique is applied to remotely measure the infrared absorption spectra of materials and to discriminate materials based on their thermal conductivities. A wavelength-tunable (7.5-8.7-μm), intensity-modulated, quantum cascade pump laser and a continuous-wave 532-nm probe laser illuminate a sample surface such that the two laser spots overlap. Surface absorption of the intensity-modulated pump laser induces a time-varying thermoelastic surface deformation, resulting in a time-varying 532-nm scattering speckle field from the surface. The speckle modulation amplitude, derived from a series of visible camera images, is found to correlate with the amplitude of the surface motion. By tuning the pump laser's wavelength over a molecular absorption feature, the amplitude spectrum of the speckle modulation is found to correlate to the IR absorption spectrum. As an example, we demonstrate this technique for spectroscopic identification of thin polymeric films. Furthermore, by adjusting the rate of modulation of the pump beam and measuring the associated modulation transfer to the visible speckle pattern, information about the

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thermal time constants of surface and sub-surface features can be revealed. Using this approach, we demonstrate the ability to distinguish between different materials (including metals, semiconductors, and insulators) based on differences in their thermal conductivities.

Body of Paper

When a diffuse surface or volume is illuminated by a laser beam, the coherent superposition of the scattered wavefronts results in a high contrast, random intensity pattern known as laser speckle [1]. While a nuisance for many coherent optical techniques such a laser radar and holography, the unique characteristics of laser speckle have enabled many applications, from blood flow imaging [2,3], to imaging through turbid media [4], to the extraction of remote speech [5] and many others [6]. Here we report on a new materials characterization technique based on speckle imaging, called photothermal speckle modulation (PSM). The approach involves measuring changes in the visible (532-nm) speckle pattern from a surface co-illuminated by a visible probe laser and an intensity-modulated long wave infrared (LWIR) pump laser (7.5-8.7-μm). The absorption of the pump laser generates a time-varying thermoelastic surface motion, consequently leading to correlated fluctuations in the speckle pattern. Critically, inherent to PSM is the interferometric sensitivity on the intensity of each speckle lobe scattering *diffusely* from a surface, and therefore, this method is distinct from other pump-probe photothermal techniques [7-10] that primarily rely on measuring the deflection of a *specular* probe beam with position sensitive detectors. Potential applications of this technique are broad and include remote chemical sensing of bulk, thin film and powder materials, and non-contact characterization of surface and sub-surface thermal properties.

A schematic of the measurement scheme is illustrated in figure 1. A tunable (7.5-8.7-μm) pump quantum cascade laser (QCL) and a visible (532-nm), single frequency probe laser are projected onto a sample under interrogation so that their laser spots overlap. Diffusively scattered probe light from the sample generates a speckle pattern which is imaged onto a visible CMOS camera. The absorption of the pump photons by the sample results in surface heating and subsequent thermoelastic deformation of the surface, both out-of-plane and in-plane, as depicted in figure 2. The pump laser power is intensity-modulated (fully on to fully off), while the probe beam is on continuously. Photothermally-induced surface deformations are excited at the frequency of the pump beam modulation, leading to speckle patterns that change in a periodic manner at the same frequency as the pump modulation. The pump modulation rate (typically 22 Hz or higher in our experiments) is selected to be faster than the time scale associated with natural speckle fluctuations due to, for example, vibrations or air currents, thus allowing high sensitivity lock-in detection at the modulation frequency. Moreover, in contrast to laser vibrometry techniques, which are only sensitive to out-of-plane surface motion, changes in the speckle pattern are effected by both the in-plane and out-of-plane surface deformations [6].

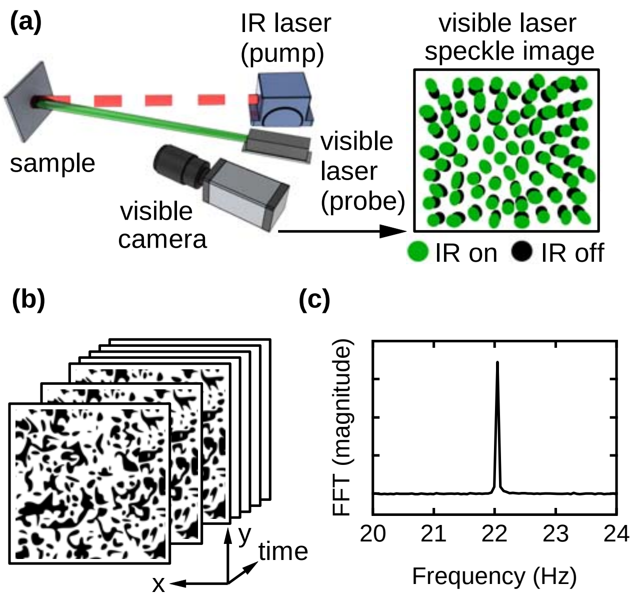

Fig. 1. PSM measurement scheme (a) (left) A tunable infrared laser (pump) and a 532-nm visible laser (probe) are projected onto the same location of a sample of interest such that their laser spots are coincident. A visible camera monitors changes in the visible laser speckle pattern as the sample's surface is periodically heated and cooled by the modulated infrared laser. (right) Illustration of the speckle pattern when pump laser is on (green) and off (black) (b) A series of speckle images are captured by the visible camera. (c) FFT spectra of each pixel through the image stack are averaged together, exposing the PSM signal which exists at the infrared modulation frequency.

In a typical measurement, ~1 mW average pump power is amplitude-modulated with a 50% duty cycle and focused to ~ 0.6 mm (full width half maximum, FWHM) spot on the surface of interest while the ~1 mW probe beam illuminates a ~3 mm FWHM spot roughly concentric with the pump. In our experiments, the sample is positioned ~1.8

meters from the pump, probe, and CMOS camera. The focusing range, focal length, and F-stop of the camera's lens are set to 1.5 m, 160 mm, and *f*/4, respectively. The lens is intentionally set to focus ~0.3 m in front of

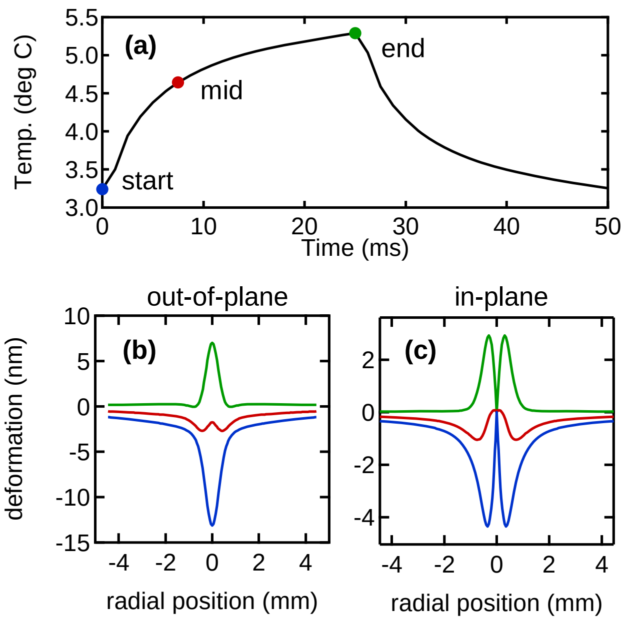

Fig 2. Photothermal surface deformation simulations using NASTRAN for a single cycle of a 1 mW average power (50% duty cycle, spot size FWHM = 0.6 mm), 20 Hz pump excitation beam incident onto a PMMA block. a) peak surface temperature response transient b) normal to surface deformations of the surface at the start, middle and end of a heating cycle c) in-plane, or radial deformations. Deformations are shown as a function of distance from the center of the heating spot.

the sample such that the average speckle lobe size is increased to approximately 5 pixels / speckle lobe. The CMOS camera records a stack of images which are processed to quantify the photothermal speckle modulation (PSM) signal. In a typical experiment,

20,000 images (frames) are collected at 500 frames per second, and each frame is 46 by 46 pixels (see figure 1b for an example speckle image stack). The magnitude of the PSM signal is obtained from this image stack using the following algorithm: first, a Fast Fourier Transform (FFT) is applied to each pixel in the image stack individually. Second, the FFT spectrum for each pixel is averaged over all the pixels resulting in a PSM spectrum for that image stack, as shown in figure 1c. As can be seen, the FFT spectrum contains a signal only at the pump modulation frequency (in this example, 22 Hz). By tuning the QCL's wavelength over a molecular absorption feature, the amplitude spectrum of the speckle modulation is found to correlate to the IR absorption spectrum. In addition to the absorption information, adjusting the rate of modulation of the pump beam and recording the associated modulation transfer to the probe beam, information about the thermal time constants of the surface can be discerned. This enables surface and even sub-surface materials discrimination based on differences in thermal conductivity.

We demonstrate the spectroscopic materials characterization capabilities of this technique on thin films of several polymers (PMMA, Teflon® AF, and PDMS), each having distinct absorption features in a wavelength range that overlaps the wavelength tuning range of our QCL. Each polymer was dissolved in a solution and applied onto a KBr substrate using standard spin-coating techniques. The samples were dried on a hot plate at 100°C for 5 minutes to remove any residual solvent. The absorption spectrum for each sample was obtained on a Fourier Transform Infrared (FTIR) Spectrometer (Bruker VERTEX 70 with a Seagull™ reflection accessory) by measuring both the transmission (T) and reflection (R) of the sample. Since KBr is transparent in the IR, the sample absorption (A) can be expressed as: A = 1-T-R (1). The surface roughness on the film

resulting from the solvent drying step was sufficient to generate a speckle pattern, therefore no further surface modifications or sample preparation steps were performed. Figure 3 shows the PSM magnitude spectrum for each material plotted versus pump wavelength, showing excellent agreement with the material's absorption spectrum.

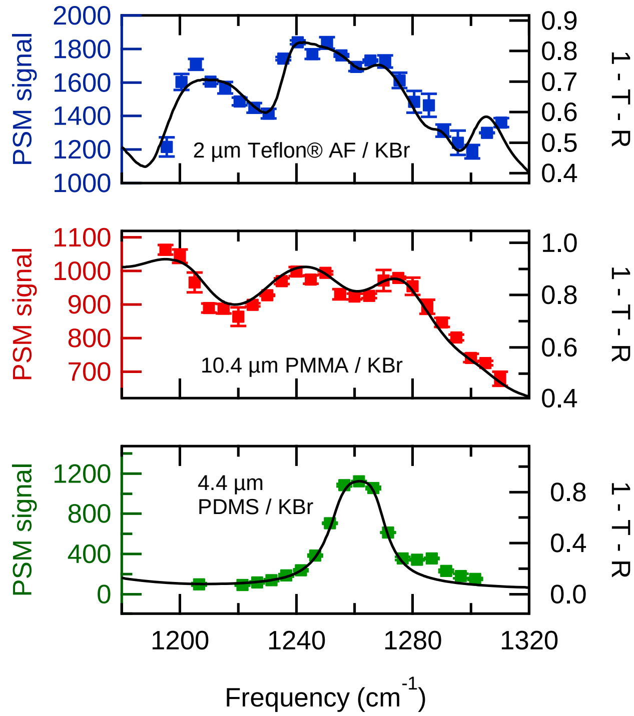

Fig. 3. PSM for spectroscopic materials analysis. PSM spectra of (top) a 2 µm Teflon® AF film on a KBr substrate, (middle) a 10.4 µm PMMA film on a KBr substrate, and (bottom) a 4.4 µm PDMS film on a KBr substrate.

A modification of this technique can be leveraged to distinguish between classes of materials based on their thermal conductivities. Instead of varying the pump laser wavelength, the frequency of the pump beam can be tuned and the PSM signal can be analyzed as a function of pump modulation frequency. The photothermal response as a function of the pump excitation frequency can be understood by considering the step

response of the material to an incident heat load over a small spot. Initially, the thermoelastic response rises nearly linearly with time before leveling off to a quasi steady-state condition. This transient behavior is well described by Beck [11], and the apparent time constant can vary from a few milliseconds for materials with high conductivity to tens of milliseconds for materials for low conductivity. When the period of excitation is long relative to the time constant, changes in the period (and frequency) of excitation produce very small changes in the peak thermoelastic response. In this region, the photothermal response vs. frequency curve is relatively flat. When the period of excitation is small relative to the time constant, the photothermal response becomes nearly proportional to the period (and inversely proportional to frequency). The transition frequency between these two regimes depends on the time constant, which is determined by the material's conductivity, specific heat and density. For higher conductivity materials, this transition occurs at higher frequencies. We demonstrate the ability to distinguish between bulk materials based on this rationale. Bars (2 mm thick by 6 mm x 10 cm) of PMMA, aluminum, and stainless steel were used as targets. The QCL wavelength and flux was fixed at 7.85 μm and $5W/cm^2$, respectively. The modulation frequency was tuned from 5 Hz through 200 Hz, while the PSM signal was analyzed for several frequencies in this range. Figure 4a shows the results of this experiment compared with simulations performed for these materials and experimental conditions using Finite Element Analysis (Nastran). As expected, aluminum (thermal conductivity of 200 W/mK) has a nearly flat response at low frequencies while PMMA (thermal conductivity of .2 W/mK) shows a 1/frequency dependence starting around 10 Hz. Note

that the response amplitude depends on a number of factors including: thermal expansion coefficient, specific heat, density and thermal conductivity.

An intriguing feature of this technique is the ability to distinguish between sub-surface properties of objects, for example, between different materials that have identical surface finishes. As a proof-of-principle demonstration, we applied a 4 μm layer of PMMA to two substrates that are IR-transmissive but have different thermal conductivities: Germanium (Ge) and Potassium Bromide (KBr). Pump light from the QCL was incident onto to each of the samples at the same fixed wavelength and average intensity (7.85 μm, 5 W/cm^2). The CMOS camera collected images at 500 frames per second with an exposure time of 0.19 milliseconds per frame. The pump light modulation frequency was tuned from 10 Hz through 200 Hz, and the PSM signal was analyzed for each frequency. The results of this experiment are displayed in Fig. 4b. For optically thin films, where the penetration depth of the pump beam is on the order of the film thickness, the photothermal surface response is still dominated by the thermal properties of the substrate, since it is the substrate which conducts most of the heat away from the surface film. Because the Ge substrate is a better thermal conductor than KBr, the PSM signal remains relatively flat to higher frequencies for Ge before it starts decreasing. Also, since the coefficient of thermal expansion is larger for KBr than for Ge, the overall signal strength is higher for KBr compared to Ge. Thus, although the surface materials for the two curves are the same (PMMA), the difference between the functional forms of the PSM signals as a function of IR pump light modulation frequency allows the two underlying substrates to be distinguished from each other due to their differing thermal conductivities.

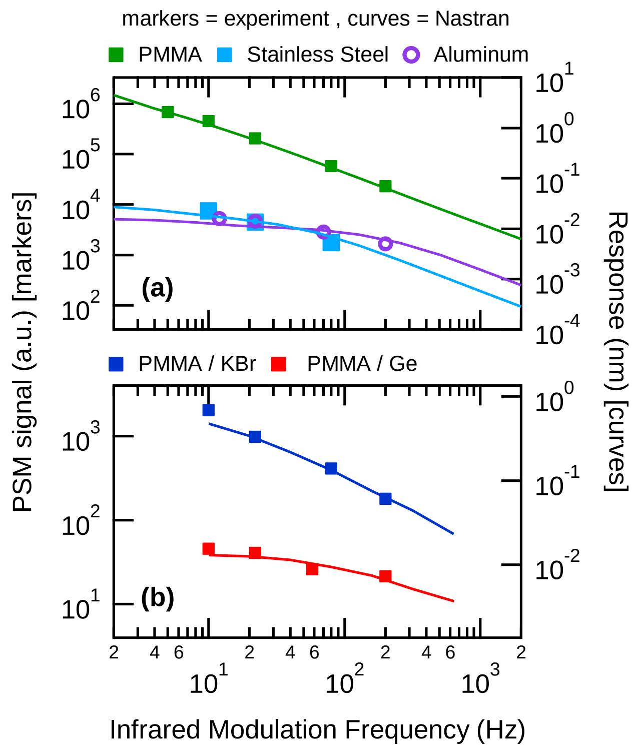

Fig. 4. Photothermal speckle modulation for thermal conductivity discrimination (a) Photothermal speckle modulation frequency responsivity data for (a) three different materials, and (b) thin PMMA films (~4 µm thick) deposited onto KBr and Ge substrates.

In summary, we have developed a new non-contact, pump-probe materials characterization method based on visible-light speckle imaging. Using this technique, IR absorption spectra and thermoelastic time constants of materials can be evaluated by analyzing speckle-pattern modulations of the probe beam induced by surface absorption of an IR pump beam. The methods described here provide new opportunities for remote sensing and other materials characterization applications, including a range of non-destructive analysis, where material composition, subsurface features, and thermoelastic

properties are of interest and can be obtained remotely and with high sensitivity using the PSM approach.

Acknowledgements

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